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C-C Bond Activation of Cyclopropane Ring in Hydrosilylation catalyzed by Wilkinson Complex

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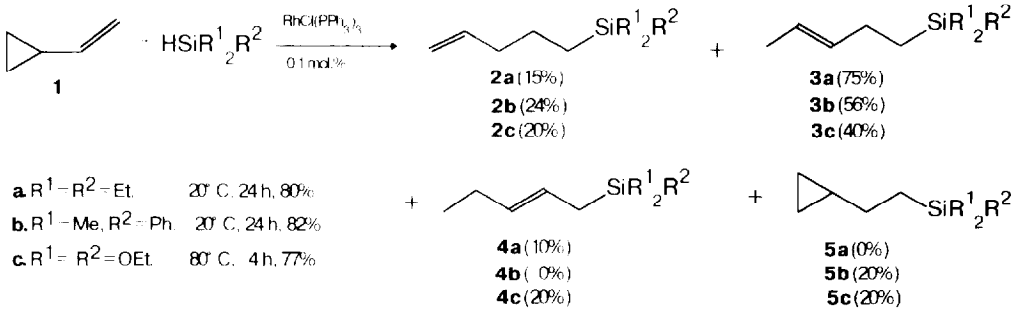
Abstract The new synthetic approach to silylated alkenes based on $RhCl(PPh_3)_3$ catalyzed hydrosilylation of vinylcyclopropanes is proposed. The mechanism of cyclopropane ring opening is discussed.

Vinylcyclopropanes are conveniently and widely used organic synthones due to their high reactivity and large variety of related synthetic transformations [1]. The chemistry of vinylcyclopropanes has expanded significantly with introduction of transition metal based catalysis [2]. However, some important catalytic reactions involving olefins that have been investigated rather extensively have not been expanded into the vinylcyclopropane field. In this paper we focused our attention on hydrosilylation, which is known as one of the most efficient synthetic routes leading to organosilanes [3].

Earlier we studied the reaction of vinylcyclopropanes with silanes [4], catalyzed by traditionally used H_2PtCl_6. The results revealed that this reaction is selectively directed to double bond, while cyclopropane ring remains intact. In the present paper we report unusual hydrosilylation with cyclopropane ring cleavage of vinylcyclopropane (**1**), 2-cyclopropylpropene (**6**) and 1,1-dicyclopropylethene (**13**) occurring in the presence of Wilkinson complex.

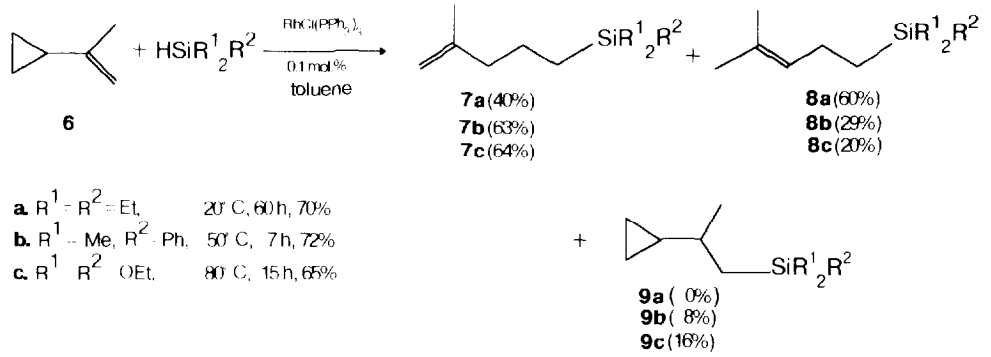
Vinylcyclopropane **1** (1.1 eq.) reacts in a sealed tube with triethylsilane (1 eq.) at room temperature, yielding the products of cyclopropane ring opening exclusively.



The corresponding 5-silyl substituted pentenes **2a, 3a** and **4a** [5] with different positions of double bond and Et_3Si group are formed in 80% yield. Raising the reaction temperature to 80°C had almost no effect on the distribution of products. Similarly the reaction of **1** with dimethylphenylsilane and triethoxysilane leads to silylated olefins **2-4**. However, in this case the competing process, hydrosilylation of the double bond, was observed. As a result, cyclopropane compounds **5b** and **5c** are formed in 20% yield. The reaction of **1** with triethoxysilane proceeds only at 80° C. The same reaction with methyldichlorosilane was very slow even at 80°C and led only to the oligomeric products.

Analogously to the regular alkenes, the hydrosilylation of vinylcyclopropanes was found to be sensitive to the steric effects of substituents at the double bond. Thus, reactions of bulky **6** and **13** with silanes slow

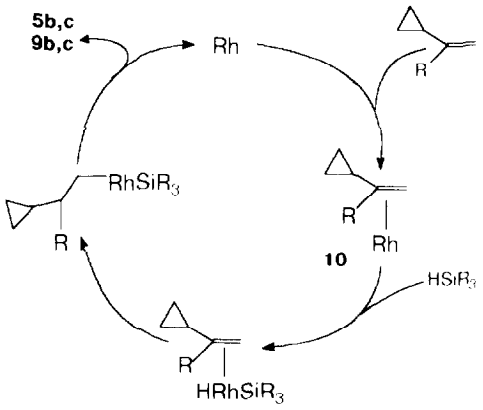
down substantially. The only ring opening products **7a** and **8a** are formed in the hydrosilylation of **6** (3 eq.) with triethylsilane (1 eq.) at room temperature



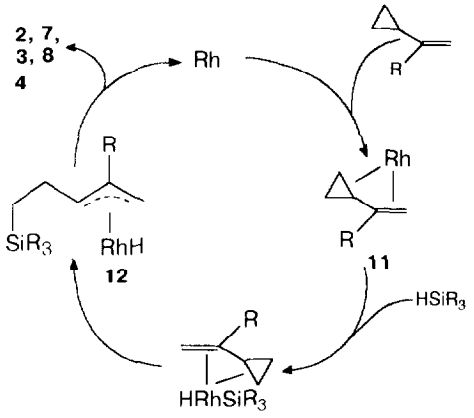
On the contrary, reactions of **6** with dimethylphenylsilane and triethoxysilane required elevated temperatures, and substantial amounts of cyclopropane products **9b,c** are formed along with cyclopropane ring opening products.

A few preliminary conclusions can be made about the mechanism of vinylcyclopropane hydrosilylation. The most common proposed mechanism for transition metal-catalysed hydrosilylation of olefins involves the key step of the olefin insertion into M-H bond of an R_3Si-M-H complex [3-7]. In some cases the second mechanism involving olefin insertion into M-Si bond as the key step was postulated to explain the formation of vinylsilanes as significant products [8].

Obviously, the formation of compounds **5** and **9** is a result of usual double bond hydrosilylation. This process most likely follows Scheme 1.



Scheme 1

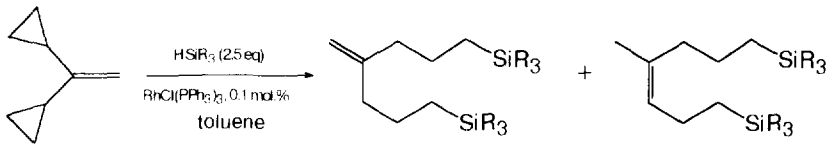


Scheme 2

The formation of terminal alkenes **2** and **7**, on the other hand, suggests that cyclopropane ring also undergoes activation during the reaction course (Scheme 2). The composition of the reaction mixture and the effect of the silane nature on the reaction direction and rate, both suggest that cleavage of C-C bond in the cycle is probably due to the migration of silyl group [8] (see Scheme 2, complex **12**). Consequently, the reductive elimination from η^3-allylic complex **12** results in the formation of silylated olefins with both terminal (**2, 7**) and internal double bonds (**3, 8**). At the same time, β-hydride elimination in **12** causes the release of rhodium complex with diene ligand, which is transformed into isomeric products **4a, c.**

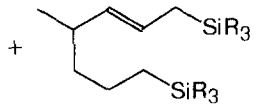
Dicyclopropylethylene **13** also undergoes hydrosilylation with the opening of both rings. Thus, reaction with triethylsilane mainly yielded **14a**, and **15a** [9]. Similarly to monocyclopropyl substrates, bringing the

reaction of **13** with triethoxysilane to completion requires heating to 80°C during 40h. Interestingly, this reaction was unexpectedly selective and terminal alkenes **14 a, b** dominate (70%) in the final mixture.



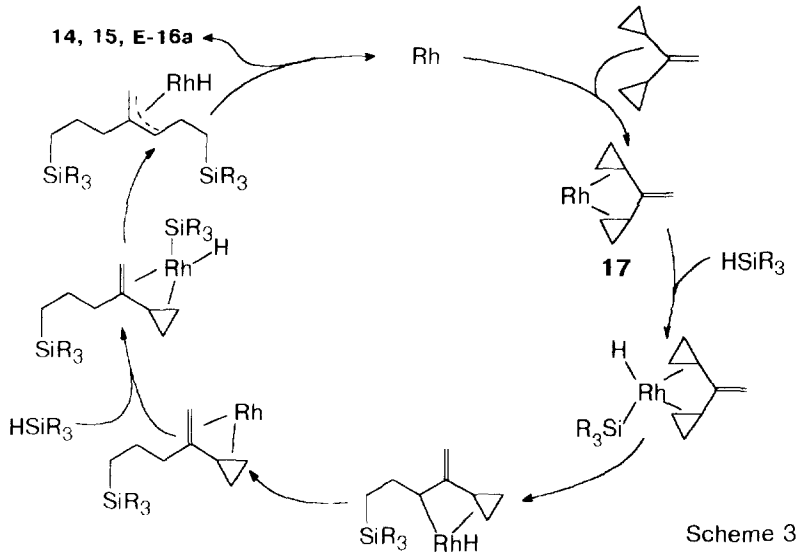
13 **14a** (69%) **14b** (70%) **15a** (26%) **15b** (30%)

a. $R^1 = R^2 = Et$, 20° C, 50 h, 81%
b. $R^1 = R^2 = OEt$ 80° C, 40 h, 60%



E-16a (5%)

Obviously, if the mechanism presented at the Scheme 2 was realized in the case of **13,** the major product of the reaction with triethylsilane would be 5-triethylsilyl-2-cyclopropylpentene-2, analogous to **3** and **8.** This compound was obtained in the specially designed experiment [10], and it was found to resist further silane addition. This suggests that it could not be the intermediate in the reaction leading to disilylated compounds **14a, b.** We suppose, therefore, that mechanism of the process includes complex with both cyclopropyl rings bound to one metal center (complex **17**, Scheme 3)



Scheme 3

In summary, in the hydrosilylation of vinylcyclopropanes carried out in the presence of Wilkinson complex ring opening dominates over the addition to C=C double bond. This reaction presents a new synthetic route to silylsubstituted alkenes, which is an alternative reaction to more common diene hydrosilylation.

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5. Reactions were carried out in the presence of 0.1 mol.% of Wilkinson complex in argon atmosphere until completion, estimated by GLC analysis of the probes, was achieved. Products were separated and purified by distillation, followed by chromatography on SiO_2 with hexane as eluent. Structures of the products were determined by ^1H and ^{13}C NMR spectroscopy, with use of homo- and heteronuclear double resonance techniques, and confirmed by calculations, based on additive schemes[6]. The spectral data of the major compounds are listed below. (**2a**): ^1H NMR (400 MHz, $CDCl_3$) δH 0.54(q, 6H), 0.57(m, 2H), 0.95(t, 9H), 1.41 (m, 2H), 2.09 (m, 2H), 4.99 (m, 2H), 5.82(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δC 3.44, 7.51, 10.99, 23.46, 37.00, 114.36, 138.98. (**E-3a**):^1H NMR δ H 0.54(q, 6H), 0.62(m, 2H), 0.95(t, 9H), 1.66(d, 3H), 2.05 (m, 2H), 5.46(m, 2H). ^{13}C NMR δC 3.37, 7.40, 11.37, 17.75, 26.79, 122.94, 134.58. (**4c**): ^1H NMR δH 0.80 (t, 3H), 1.15(t, 9H), 1.53(d, 2H), 2.00(m, 2H), 3.75(q, 6H), 5.26(m, 2H). ^{13}C NMR δC 11.96, 13.89, 18.11, 20.21, 58.17, 121.79 130.93. (**5c**) ^1H NMR δH -0.10(m, 2H), 0.28(m, 2H), 0.61(m,1H), 0.62 (m, 2H), 1.11(t, 9H), 1.21(m, 2H), 3.70(q, 6H). ^{13}C NMR δC 4.46, 4.46, 10.12, 13.87, 18.25, 27.99, 58.24. (**7c**): ^1H NMR δH 0.54(m, 2H), 1.15(t, 9H), 1.48(m, 2H), 1.61(s, 3H), 1.96(t, 2H), 3.74(q, 6H), 4.59(d, 2H). ^{13}C NMR δC 9.85, 18.00, 18.20, 20.78, 41.04, 58.21 110.08, 145.41. (**8c**): ^1H NMR δ H 0.59(s, 3H), 1.15(t, 9H),1.52(s, 3H), 1.59(s, 6H), 2.02(m, 2H), 3.74(q, 6H), 5.09(t, 1H). ^{13}C NMR δC 10.76, 18.20, 21.11, 22.20, 25.52, 58.21, 127.03, 130.10. (**9c**): ^1H NMR δH 0.00(m, 2H), 0.04(m, 1H), 0.33(m, 1H), 0.53(m, 1H), 0.60(m, 1H), 0.83(m,1H), 0.87(m, 1H) 1.01(d, 3H), 1.18(t, 9H), 3.76(q, 6H). ^{13}C NMR δ C 3.96, 4.26, 18.13, 18.31, 20.86, 22.16, 34.29, 58.05. Spectral data confirm the structures suggested for other compounds.
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9. Spectral characteristics of **14a**: ^{13}C NMR δ C: 3.48, 7.52, 11.26, 11.26, 23.30, 23.30, 40.36, 40.36, 109.13, 149.69. **Z-15a**: ^{13}C NMR δ C: 3.48, 7.52 11.46, 12.33, 22 13, 22.51, 23.40, 35.96, 128.92, 133.56. **E-15a**: ^{13}C NMR δ C: 3.48, 7.52, 11.09, 11.95, 15.78, 22.21, 29.87, 44.03, 128.11, 133.35. **E-16a** ^{13}C NMR δ C: 3.48, 7.52, 11.60, 17.35, 21.40, 21.79, 37.01, 42.02, 124.16, 135.14. Spectra NMR ^1H correspond to suggested structures. Spectral data confirm the structures suggested for **14b** and **15b**.
10. 5-Triethylsilyl-2-cyclopropylpentene-2 was obtained by the reaction of (1-methyl-1-cyclopropylmethylene)cyclopropane with triethylsilane in the presence of Wilkinson catalyst. ^1H NMR δ H 0.51(m, 4H), 0.54(q, 6H), 0.64(m, 2H), 0.96(t, 9H), 1.41(s, 3H), 1.64(m, 1H), 2.16(m, 2H), 5.27(t, 1H).

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